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Poly(D,L-lactide)/Hydroxyapatite Composite Tissue Engineering Scaffolds prepared by Stereolithography

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Introduction

Hydroxyapatite (HAP) is a major component of bone and has osteoconductive and -inductive properties. It has been successfully applied as a substrate in bone tissue engineering, either with or without a biodegradable polymer such as polycaprolactone or polylactide.

Recently, we have developed a stereolithography resin based on poly(D,L-lactide) (PDLLA) and a non-reactive diluent, that allows for the preparation of tissue engineering scaffolds with designed architectures. In this work, designed porous composite structures of PDLLA and HAP are prepared by stereolithography.

Materials and Methods

HAP powder (particle size <15 μm) was dispersed at 60 °C in poly(D,L-lactide) dimethacrylate macromer (molecular weight 1.2 kg/mol, end-group conversion 96%). Then, a solution of Lucirin TPO-L photo-initiator and Orasol Orange G dye in N-methyl-2-pyrrolidone (NMP) was mixed in. The final resin composition was 63 wt% macromer, 19 wt% HAP, 15 wt% NMP, 3.1 wt% Lucirin photo-initiator, 0.06 wt% dye and 0.2 wt% inhibitor. This resin was used to prepare designed porous structures with a commercial stereolithography setup (Envisiontec Perfactory). The exposure time was 3.5 s per 25 μm thick layer, at a blue light intensity of 20 mW/cm^2. After extraction of diluent, dye and unreacted photo-initiator, the resulting PDLLA/HAP structures were analysed by μCT, XPS and SEM.

Results and Discussion

The stereolithography resin was a homogeneous dispersion that showed no settling of HAP particles on the timescale of days.

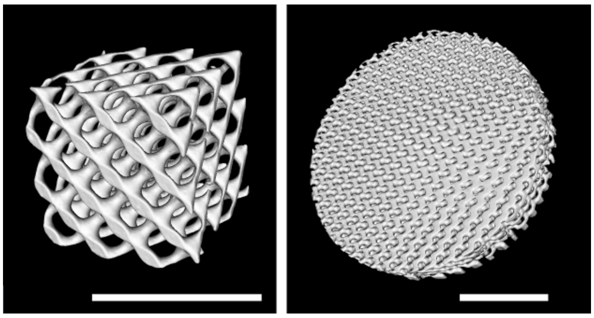

Figure 1: μCT visualisations of two different PDLLA/HAP scaffolds built by stereolithography (scalebar is 5 mm)

Different composite porous structures were prepared from this resin by stereolithography, as shown in Figure 1. The left cubic scaffold has a diamond architecture with a porosity of 74% and an average pore size of 707 μm (determined by μCT). The right disk-shaped scaffold has a gyroid architecture and is 53% porous with an average pore size of 310 μm.

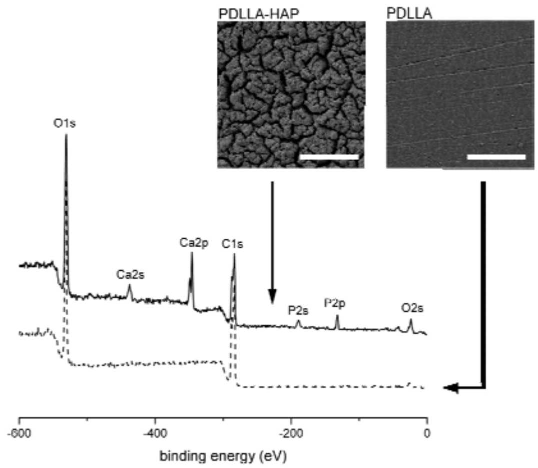

Figure 2: XPS-analysis of photo-crosslinked PDLLA networks, with and without HAP. The scalebars in the SEM insets represent 200 μm.

The XPS-results shown in Figure 2 reveal the presence of Ca and P at the surface of the photo-crosslinked composite structures. The Ca:C molar ratio at the surface was 1:8.8, compared to 1:17.6 for the resin components. The SEM-images confirm the higher HAP concentration at the surface, as they show HAP particles sticking out of the network surface.

The combination of an open porous architecture and the availability of HAP at the surface will make these structures most suited for bone tissue engineering.

Conclusions

Designed porous PDLLA/HAP composite structures were prepared by stereolithography. The ceramic particles are exposed to the surface, allowing the interaction of cells with HAP.

Acknowledgements

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